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DATE: August 11, 2005

SUBJECT: A PARTITION OF PESTICIDE LOADS IN MAJOR SUBBASINS IN THE SACRAMENTO RIVER WATERSHED–PRELIMINARY RESULTS OF STUDY 227

Abstract

The Department of Pesticide Regulation (DPR) conducted a monitoring study during the storm event of January 26 to February 1, 2005, to evaluate the relative contributions of major subbasins to pesticide loads in the Sacramento River. Five pesticides and one triazine degradation product were detected. The three most widely detected pesticides were diuron, diazinon, and simazine, which were found in all streams monitored. The cumulative export from the Sacramento River watershed of the three pesticides was 95.1, 13.8, and 13.1 kg, respectively. Two other pesticides, bromacil and hexazinone were only detected in subbasin streams of Cross Canal and Colusa Basin Drain, with loads ranging from 0.25 to 7 kg. Diamino chlorotrazine (DACT), a simazine degradation product, was only detected at Cross Canal with a total export of 2.1 kg. The major contributing subbasin was the Sacramento River above Colusa. Based on the temporal relationship between pesticide peak detection and the occurrence of precipitation, the estimated mean pesticide travel time from the field to the outlets of the subbasins was >24 hour. Similarly, the estimated travel time from the field to the main outlet of the Sacramento River at Alamar Marina was >72 hour. The estimated mean velocity of pesticides in the Sacramento River was 1.9 km/hour. Results of this study captured the general trend of pesticide transport during the storm event and provided useful information for development of future sampling plans.

Introduction

Movement of pesticides by surface water runoff during storm events is a primary transport pathway for pesticide movement from fields to streams. There are approximately 2.1 million acres of agricultural land in the Sacramento Valley, which received pesticide applications in excess of 8,000 tons per year according to the Pesticide Use Report (PUR) <http://www.cdpr.ca.gov/docs/pur/purmain.htm> of DPR. Pesticide movement to waterways in the Sacramento Valley is a prime concern in water quality management for the Sacramento River watershed.

Numerous monitoring studies have evaluated pesticide contamination of the Sacramento River and its tributaries (Domagalski, 1996; Nordmark et al., 1998; Domagalski et al., 2000; Dileanis et al., 2002). These studies revealed the presence of many pesticides in Sacramento Valley surface waters, especially organophosphorus insecticides and preemergent herbicides (Spurlock, 2002; Guo et al., 2004). Adequately characterizing the source and transport of pesticides in the Sacramento Valley is an essential component of mitigation attempts to reduce pesticide loading of surface water. The objective of this monitoring study was to determine the relative contributions of pesticide load to the Sacramento River from its major subbasins during winter storm events. The study was performed in conjunction with a watershed modeling project to further the understanding of pesticide transport in the Sacramento River watershed, and to provide calibration data for the watershed modeling effort.

Materials and Methods

The study was conducted from January 26 to February 1, 2005, after application of dormant spray pesticides started in the Sacramento River watershed. Surface water samples were taken from five monitoring sites located at outlets of the major subbasins and the watershed (Figure 1). Four of these sites represent subbasin outlets of the (1) Sacramento River above Colusa, (2) Colusa Basin, (3) Feather River, and (4) the Natomas Cross Canal. A fifth site, the Alamar Marina, represents the main stem of the Sacramento River. The main stem site characterizes the total load of pesticides to the Sacramento River from the upstream five subbasins, excluding the American River. Pesticide loading from the American River subbasin is negligible due to the extremely low use of dormant spray pesticides in the area. For example, the American River subbasin historically received <0.05 percent of the total agricultural use of diazinon in the Sacramento River watershed based on PUR data. The subbasin of Butte/Sutter Basin, one of the five major subbasins above the Alamar Marina, was not monitored due to the difficulty in locating a suitable site for accurately characterizing drainage. Table 1 (attached) lists the name, location, corresponding subbasin/watershed, and source of stream gage data for the monitoring sites.

Surface water sampling was conducted twice daily at each site for the first two days following the initial storm of January 26 to catch the rapid change of pesticide concentration expected. The sampling frequency was then reduced to once daily for the rest of the sampling event. A center channel grab water sample was taken from bridges or road crossings using a 4.2-L stainless steel Kemmerer sampler (Wildlife Supply Company), and was then split into two 1-L amber glass bottles for separate pesticide screening analyses. Due to lack of accessibility to the river center, water samples at the Feather River site were collected directly with the amber glass bottles from a depth of at least one meter using a telescoping rod from the shore. All samples were sealed with Teflon-lined lids and placed on wet ice until transferred to the DPR's facility in West Sacramento. The samples were then stored at 4°C until delivered to laboratory for chemical analysis. For each sampling event, general water quality parameters of pH, temperature, dissolved oxygen, and specific conductance was measured in situ at each site. The chemical analysis of the water samples were performed by the California Department of Food and Agriculture Center for Analytical Chemistry using the methods #46.0 and #62.9 for two pesticide screening analyses, respectively. The analytes and their major physicochemical properties and analytical reporting limits are provided in Table 2 (attached).

Daily pesticide load was calculated based on the measured pesticide concentration and stream flow rate using the following equation:

$$Y(t) = 0.00245\,C(t)F(t)$$

where *Y(t)* is the estimated pesticide load (kg d^{-1}) for day *t*, *C(t)* is the pesticide concentration (μg L^{-1}), *F(t)* is the stream flow rate (cfs, or cubic foot per second), and 0.00245 is a conversion factor. The laboratory used two reporting notations for samples with concentrations lower than the method reporting limit: trace and none detected. For samples with a reported concentration of trace, the pesticide load was calculated assuming one half of the reporting limit. For samples with a reported concentration of none detected, pesticide load was assumed to be zero.

Results and Discussion

Water Quality Parameters

The water quality parameters measured at the monitoring sites are presented in Figure 2. The pH for all sites was close to neutral, ranging from 7.2 to 8.0. The specific conductance varied between 100 to 600 μs/cm, with highest values found for Colusa Basin Drain (≥387 μs/cm) and lowest for the Feather River (≤123 μs/cm). The total dissolved oxygen varied from 7.29 to 10.8 mg/L, and was consistently higher for the main stem of the Sacramento River and the Feather River, and lower for the Colusa Basin Drain and Cross Canal. The mean values of dissolved oxygen were 10.26 and 10.10 mg/L for the Sacramento River and Feather River, respectively, and were 7.74 and 8.31 for Colusa Basin Drain and Cross Canal, respectively. Water temperature was rather consistent for all streams during the sampling event, with an average of 10.6°C (Figure 2).

Pesticide Load

Out of 27 analytes (Table 2), five pesticides and one breakdown product of triazine were detected. These include diazinon, simazine, diuron, hexazinone, bromacil, and diamino chlorotriazine. Figure 3 (attached) shows loading of these pesticides over time during the monitoring period, and Table 3 (attached) summarizes the partition of the loads among the tributaries and main stem of the Sacramento River.

Diuron was the most widely detected pesticide and it was found at all subbasins as well as in the main stem of the Sacramento River (Figure 3). Most of diuron load in the Sacramento River came from the subbasin of the Sacramento River above Colusa. The observed peak load of diuron at this site was greater than the peak load measured at the Alamar Marina Dock (Table 3). Colusa Basin Drain contributed 26.6 kg of diuron to the Sacramento River during the sample collection period, compared to 4.9 kg and 1.4 kg from the Feather River and Cross Canal, respectively. The total export of diuron from the Sacramento River at Alamar Marina during the sample collection period was 95 kg during the seven-day sampling period (Table 3).

Diazinon was also detected in all monitoring sites. The load of diazinon from Cross Canal, however, was negligible (~0.1 kg). Most of the contribution of diazinon in the Sacramento River was also from the subbasin of the Sacramento River above Colusa (Figure 3). Diazinon contributions from the Feather River and CBD were similar, being 4.7 and 4.0 kg, respectively. The cumulative export of diazinon from the Sacramento River watershed was about 14 kg during this storm event (Table 3).

Simazine was the third most frequently detected pesticide. The largest load of simazine was again from the subbasin of the Sacramento River above Colusa (Figure 3), which reached about 19 kg. Colusa Basin Drain contributed about 13 kg simazine to the Sacramento River, and contributions from the Cross Canal and Feather River were both less than 0.2 kg.

The fact that the observed loads for the three pesticides of diuron, diazinon, and simazine at the Colusa site, were all greater than those measured at the Alamar Marina Dock indicate a high possibility that appreciable attenuation occurred during pesticide traveling between these two sites. It is also likely, however, that the discrepancy in load was attributable to sampling variability due to the spatial and temporal differences at the two sampling locations. Additional studies would be required to further validate and characterize any potential in-stream attenuation of pesticides in the Sacramento River.

For the two other pesticides, bromacil and hexazinone, and the breakdown product of triazine DACT, they were only detected in the subbasins of CBD and Cross Canal (Figure 3). These contaminants may be diluted in the main stem of the Sacramento River that their concentrations were below the detection limits. Approximately one kg of bromacil was exported from the Colusa Basin Drain and Cross Canal combined (Table 3). The export of hexazinone was 7.0 kg from the Colusa Basin Drain and was 0.25 kg from Cross Canal. DACT was only detected in Cross Canal at 2.1 kg.

It has been shown that rainfall-driven winter pesticide loads in the Sacramento River are directly related to pesticide use and precipitation (Guo et al., 2004). The 2005 PUR data are not yet available; therefore use of these pesticides (and others analyzed) in the watershed cannot be evaluated at this time. Examine of the precipitation data in the area indicated that precipitation at the Gerber station (CIMIS 8), located in the subbasin of the Sacramento River above Colusa, was significantly higher than the other stations (Figure 1 and Table 4). The cumulative precipitation from January 24 to 29 reached 5.41 cm for the Gerber station, which was more than twice those observed for the other stations (<2.34 cm). It is likely that the greater contribution of pesticides from the Sacramento River above Colusa observed during this storm event was at least partly attributable to higher precipitation in this subbasin. It must be noted that the highest export of pesticide from a subbasin does not automatically qualify it as the most vulnerable subbasin requiring mitigation, because the area of drainage in each subbasin varies. A more creditable criterion we believe would be the intensity of pesticide export, which would be related to both the drainage area and amount of pesticide use in the subbasin. In addition, effect of precipitation on export intensity should also be considered. As noted above, in this particular storm event, SR above Colusa received significantly higher precipitation than the other subbasins (Table 4). The results of this study must be understood with this difference in mind.

Pesticide Travel Time

Estimation of pesticide travel time from the field to the waterways can be achieved by examining the temporal relationship of pesticide peak in the streams to the occurrence of the storm event. Precipitation occurred from January 24 through January 29, with the major storm falling on January 26 in most of the subbasins (Table 4). The earliest detection of pesticide peak in the streams, however, was only made on January 28 at the most upstream location of the Sacramento River at Colusa (Figure 3). For the other sites, the peaks of pesticide load were not detected until after January 29 or 30th (Figure 3). These results indicated that it took at least two days for the pesticides to move from the field to the outlets for both the smaller subbasins and the main Sacramento River watershed. The travel times observed in this study are specific to the conditions of precipitation in this study.

Comparison of peak detection time for the two main stem Sacramento River sites provides a way to estimate the travel time of pesticides within the Sacramento River. There was a two-day delay between the peaks of pesticide load detected at the Colusa site and those at the downstream Alamar Marina site for all pesticides (Figure 3). The estimated river distance from Colusa to the Alamar Marina Dock is 92 km. Thus the travel speed of the pesticides within the Sacramento River was about 1.9 km/hour. In theory, pesticides are not ideal tracers of water flow, because their movement in the river would be retarded to some extent due to adsorption/desorption to sediment. Neglecting the retardation, the dissolved pesticides would be traveling at the same speed as the water movement in the Sacramento River. It is therefore inferred that the flow rate of the Sacramento River in the segment between Colusa and Alamar Marina was about two km/hour. Since our samples were taken close to the central channel of the river, the integrated flow rate for the entire cross section of water column for the Sacramento River would be slower.

Acknowledgement

The authors would like to express their thanks to Nina Bacey for her help in sampling, and to chemists of the California Department of Food and Agriculture for their superior service in laboratory analyses of the water samples.

Attachment

bcc: Guo Surname File (w/Attachment)

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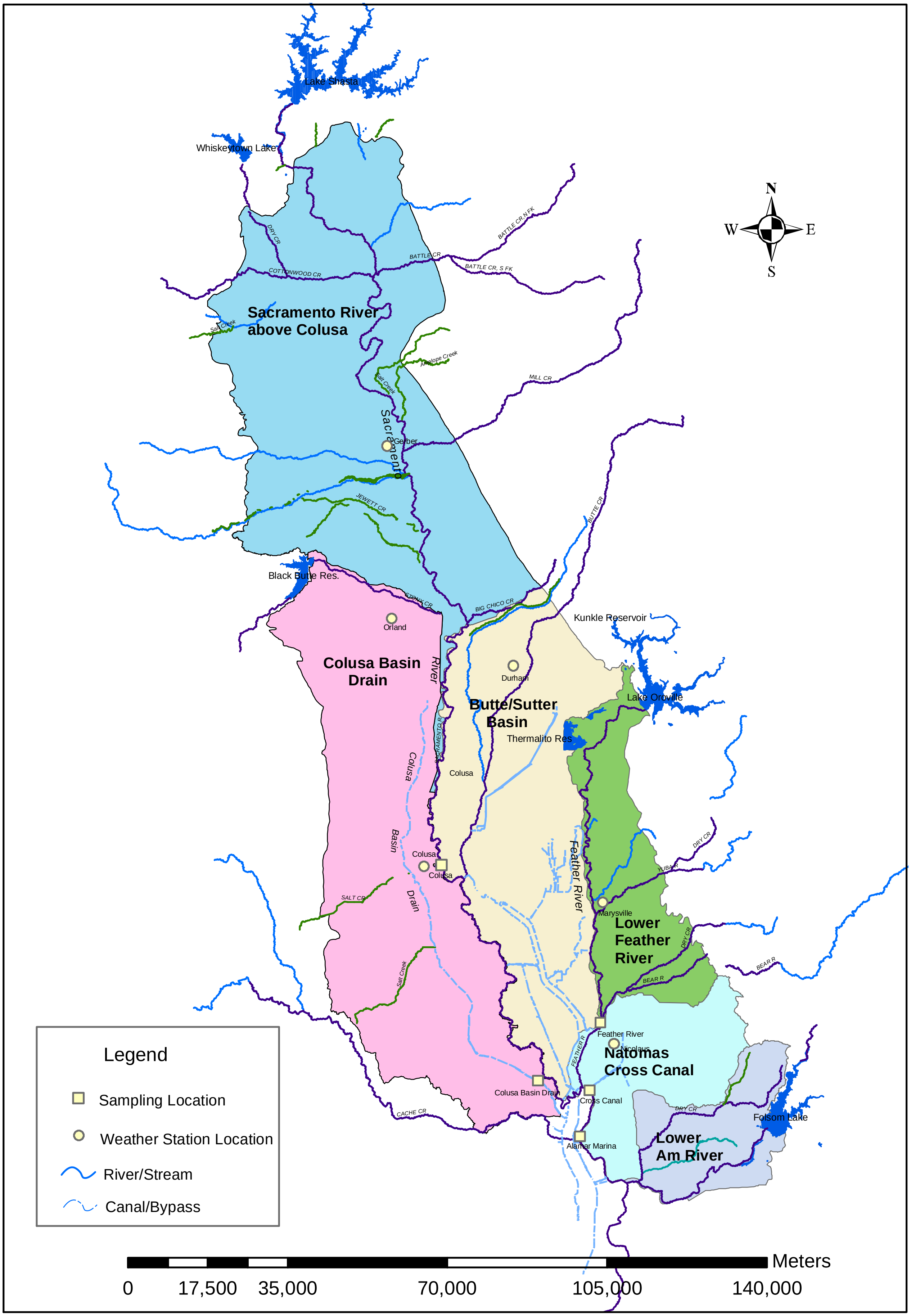

Figure 1. Sampling and weather station locations for the Sacramento River watershed.

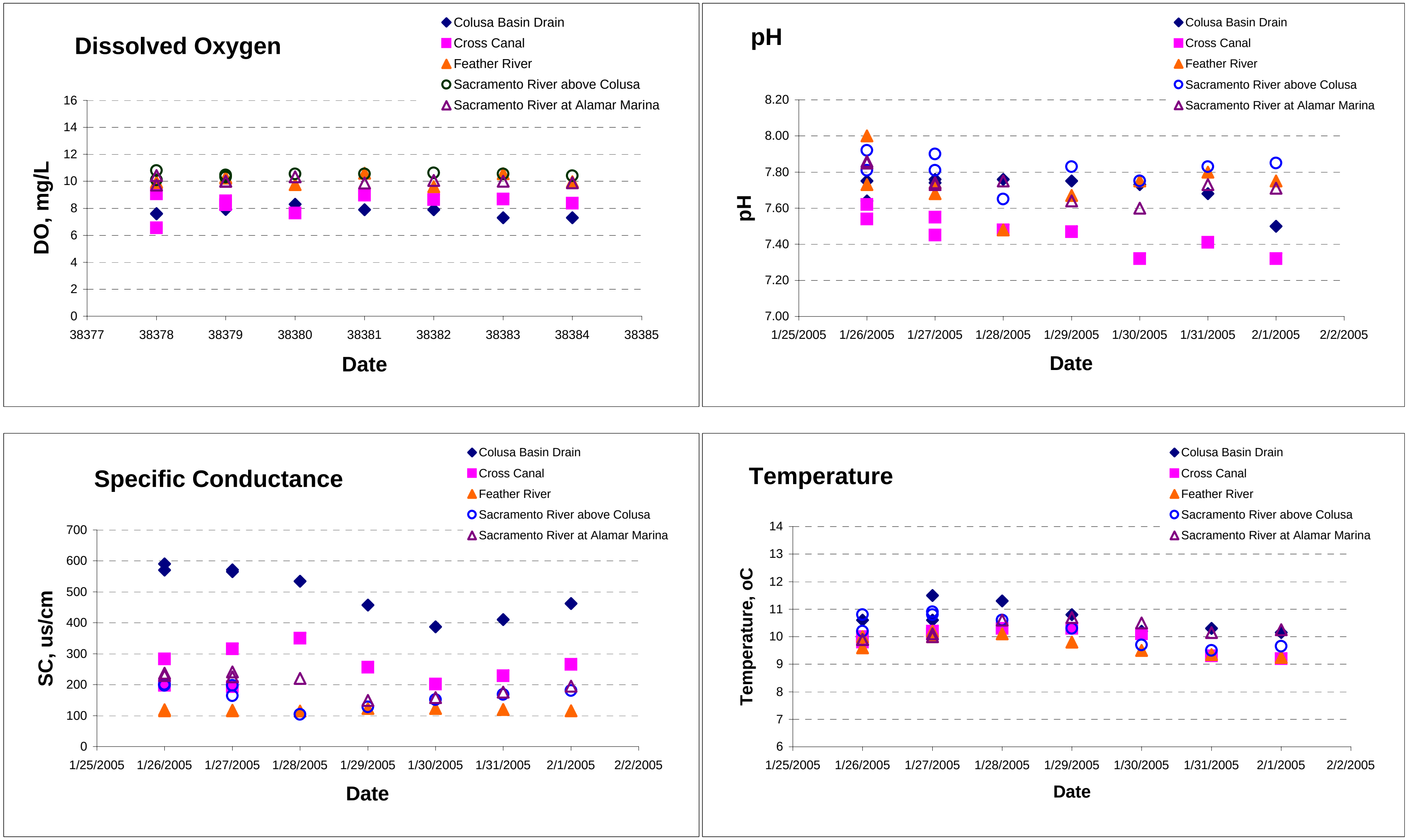

Figure 2. The measured water quality parameters for the major subbasins and the main outlet of the Saramento River watershed during the storm event of January 26 to Feburary 1, 2005.

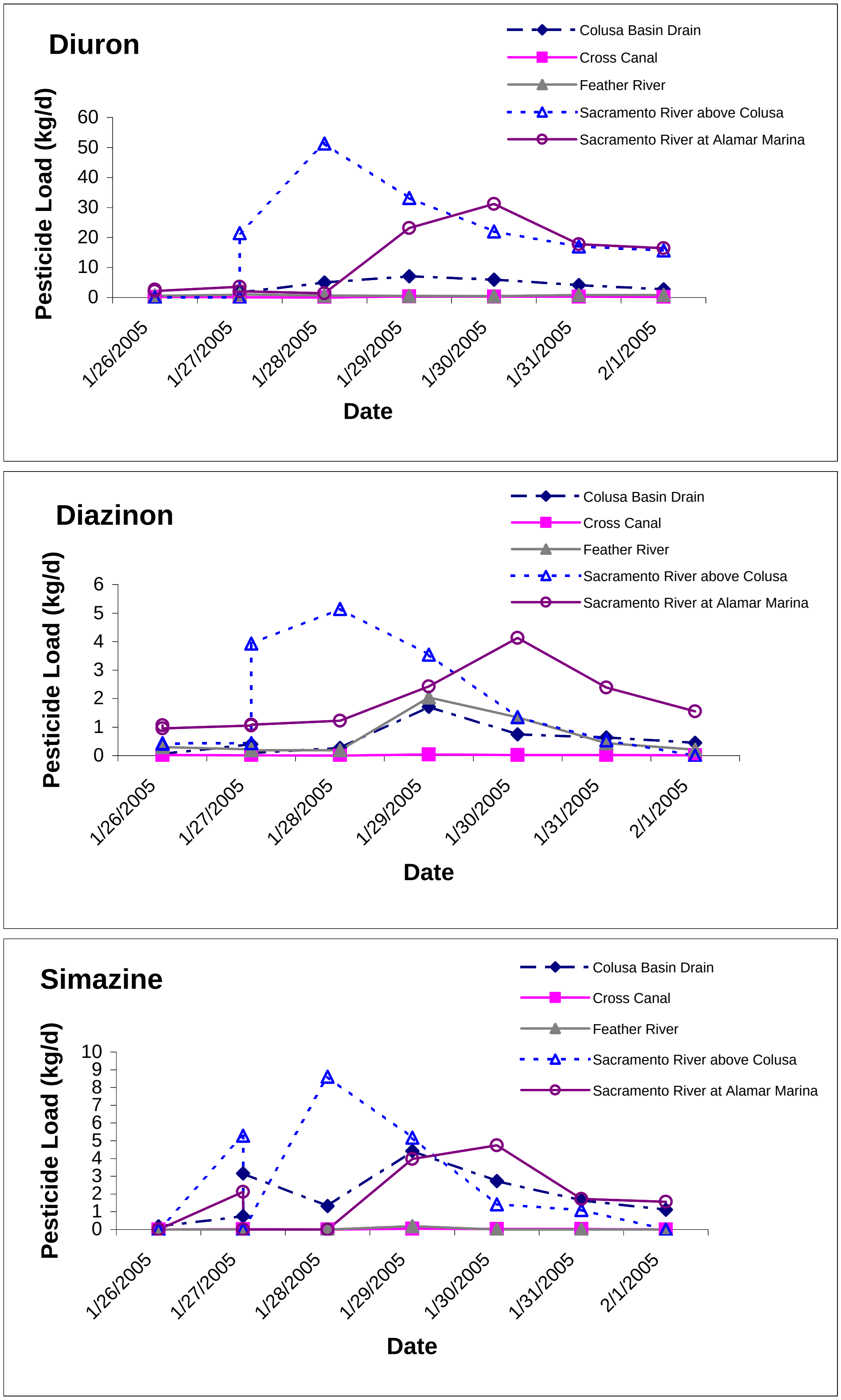

Figure 3. Pesticide loading over time from the major subbasins and at the main outlet of the Sacramento River watershed at Alamar Marina during the storm event of January 26 to February 1, 2005.

Table 1. Sampling sites and their corresponding subbasin/watershed for storm event monitoring of January 26 to February 1, 2005.

Site Name	Latitude	Longtitude	Subbasin/watershed	Gage station*
Colusa Basin Drain at Rd. 99E	38.81219	-121.77319	Colusa Drain	CDR
Cross Canal at Garden Hwy.	38.78079	-121.60314	Natomas Cross Canal	Manually Gauge
Feather River near Hwy. 99	38.89811	-121.58693	Feather River	GRL + MRY + BRW
Sacramento River at Colusa	39.21453	-121.99907	Sacramento River above Colusa	COL
Sacramento River at Alamar Marina	38.67479	-121.62650	Sacramento River watershed	VON

* The three letter designation of real-time discharge stations operated by California Department of Water Resources; discharge data available at http://cdec.water.ca.gov/selectQuery.html.

Table 2. List of chemicals analyzed for the storm event sampling of January 26 to Febuary 1, 2005 in the Sacramento River watershed.

Chemical	Koc, mL/g	t1/2, day	Solubility, mg/L	Report limit, µg/L
Ethoprop	161	34	843	0.05
Diazinon	1520	32	60	0.01
Disulfoton	1345	37	12	0.04
Chlorpyrifos	9930	43	1.18	0.01
Malathion	1200	9	130	0.04
Methidathion	400	7	240	0.05
Fenamiphos	100	50	700	0.05
Azinphos methyl	882	44	28	0.05
Dichlorvos	30	7	10000	0.05
Phorate	1057	37	50	0.05
Fonofos	1920	37	13	0.04
Dimethoate	20	7	39800	0.04
Methyl Parathion	5100	5	55	0.03
Tribufos	650	12	4.5	0.05
Profenofos	-	-	-	0.05
Atrazine	147	64	33	0.05
Simazine	140	89	6.2	0.05
Diuron	477	90	42	0.05
Prometon	95	1300	720	0.05
Bromacil	13	120	700	0.05
Prometryn	383	76	33	0.05
Hexazinone	41	79	29800	0.05
Metribuzin	52	47	1000	0.05
Norflurazon	353	163	34	0.05
DEA	-	-	-	0.05
ACET	-	-	-	0.05
DACT	-	-	-	0.05

* Sources for chemical property values are 1) USDA, ARS Pesticide Properties Database at http://www.arsusda.gov/rsml/ppdb.html; 2) Pesticide Information Profile EXTONET, University of California at Davis, Oregon University, Michigan State University, Cornell University and the University of Idaho at http://extoxnet.orst.edu/pips/ghindex.html; and 3) Pesticide Action Network North America, PAN Pesticides Database at http://www.pesticideinfo.org/Index.html.

Table 3. Summary of pesticide load partitioning in the major subbasins of the Sacramento River waterhsed measured during the storm event of January 26 to February 1, 2005.

	Pesticide load, kg					
Subbasin/watershed	diuron	diazinon	simazine	hexazinon	bromacil	DACT
Colusa Basin	26.57	4.10	13.37	7.03	0.40	0
Natoma Cross Canal	1.44	0.11	0.12	0.25	0.64	2.11
Feather River	4.90	4.72	0.20	0	0	0
Sacramento River above Colusa	149.95	13.19	18.95	0	0	0
Sacramento River at Alamar Marir	95.14	13.80	13.06	0	0	0

Table 4. Precipitation measured at representative weather stations of the subbasins in the Sacramento Valley during the strom event of January 26 to to February 1, 2005. Locations of the stations are shown on Figure 1.

	Station	Network/	Precipitation, cm										
Basin/subbasin	name	operator[a]	1/23	1/24	1/25	1/26	1/27	1/28	1/29	1/30	1/31	2/1	Total
Colusa Drain	Orland	CIMIS 61	0.00	0.00	0.03	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.10
	Colusa	CIMIS 32	0.00	0.05	0.61	0.51	0.43	0.30	0.00	0.00	0.00	0.00	1.91
	Davis	CIMIS 6	0.00	0.03	0.15	0.74	0.30	0.43	0.03	0.00	0.00	0.00	1.68
Natomas-Cross Canal	Nicolaus	CIMIS 30	0.00	0.03	0.03	0.94	0.23	1.12	0.00	0.00	0.00	0.00	2.34
Butte/Sutter Basin	Durham	CIMIS 12	0.00	0.00	0.46	0.81	0.08	0.38	0.00	0.00	0.00	0.00	1.73
Feather River	Marysville	NOAA 5385	0.00	0.00	0.03	0.64	0.38	0.79	0.36	0.00	0.00	0.00	2.18
Sacramento River above Colusa	Gerba	CIMIS 8	0.00	0.03	0.99	3.25	0.36	0.79	0.00	0.00	0.00	0.00	5.41

[a] CIMIS stands for California Irrigation Management Information System; NOAA stands for National Oceanic and Atmospheric Administration.